

The Infrared Absorption Band and Vibronic Structure of the Nitrogen-Vacancy Center in Diamond

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The negatively charged nitrogen-vacancy (NV^-) color center in diamond has generated much interest for use in quantum technology. Despite the progress made in developing their applications, several questions about the basic properties of NV^- centers remain unresolved. In particular, knowledge of the phonon modes of the 1A_1 electronic state is key for understanding the optical pumping process. Using pump-probe spectroscopy, we measured the phonon sideband of the $^1E \rightarrow ^1A_1$ electronic transition in the NV^- center. From this we calculated the $^1E \rightarrow ^1A_1$ one-phonon absorption spectrum and found it to differ from that of the $^3E \rightarrow ^3A_2$ transition.

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The nitrogen-vacancy (NV) center in diamond (Fig. 1a) is a color center consisting of a substitutional nitrogen atom in the diamond crystal lattice adjacent to a missing carbon atom (a vacancy). NV centers have C_{3v} point-group symmetry and have discrete electronic energy states between the diamond valence and conduction bands. The negatively charged NV^- center can be optically spin-polarized and read out, and it has a long ground-state transverse spin relaxation time at room temperature [1, 2]. These properties make NV^- centers useful in a variety of applications including electric and magnetic field sensing [3–6], rotation sensing [7–9], quantum computing [10, 11], quantum cryptography [12, 13], and sub-diffraction-limited imaging [14–16]. Despite the progress made on developing these applications, the complete NV^- energy level structure and vibronic structure are unknown.

Figure 1b shows a simplified NV^- energy-level diagram as confirmed by experiment. The triplet-triplet ($^3A_2 \leftrightarrow ^3E$) and singlet-singlet ($^1E \leftrightarrow ^1A_1$) energy differences are known to be 1.945 eV (637 nm) and 1.190 eV (1042 nm), respectively [17–20]. However, neither where these energy states lie with respect to the diamond valence and conduction bands nor the triplet-singlet ($^3A_2 \leftrightarrow ^1A_1$ and $^1E \leftrightarrow ^3E$) energy differences are known directly [21, 22]. Theoretical calculations predict the existence of additional energy states ($^1E'$ and $^1A_1'$), but disagree on their energies (see Refs. [23–27] and references therein). Prior experiments and *ab initio* calculations studied the phonon sidebands (PSBs) for the $^3A_2 \rightarrow ^3E$ and $^3E \rightarrow ^3A_2$ transitions [17, 28–31]. The $^1E \rightarrow ^1A_1$ and $^1A_1 \rightarrow ^1E$ PSBs have not been studied theoretically, and only the $^1A_1 \rightarrow ^1E$ transition had been

measured prior to this work [18–20].

A more complete experimental picture of NV^- properties can provide insight for applications and validate theoretical models of NV^- center attributes. We attempt to fill the gaps in the knowledge of NV^- properties by measuring the $^1E \rightarrow ^1A_1$ PSB and searching for previously unobserved transitions. Finding the $^1E \rightarrow ^1E'$ zero-phonon line (ZPL) would resolve the disagreement on the predicted $^1E'$ energy. The $^1E \rightarrow ^1A_1$ PSB yields information about the 1A_1 phonon modes, which are also of interest. The spin-orbit interaction mixes the 3E and 1A_1 states, resulting in triplet-singlet intersystem crossing (ISC). This enables non-radiative decay from the nominally 3E state to the nominally 1A_1 state. The ISC rate is comparable to the $^3E \rightarrow ^3A_2$ spontaneous decay rate [32, 33] and is an important factor in the optical pumping process to the 3A_2 $m_s = 0$ state. Measuring the 1A_1 phonon modes could provide insight on the mechanism used for NV^- spin polarization and read-out. Furthermore, the accepted group theoretical model of NV^- predicts 3A_2 and 1A_1 to have the same electronic configuration, meaning they should have the same phonon modes. A comparison between the $^3A_2 \rightarrow ^3E$ and $^1E \rightarrow ^1A_1$ PSBs should be sensitive to differences between the 3A_2 and 1A_1 configurations.

In our experiment, we populated the metastable 1E state using pump-laser light and measured transmission of probe-laser light through a diamond sample containing an ensemble of NV^- centers (Fig. 1b and Fig. 2). We determined the probe transmission through the diamond with and without NV^- centers in the 1E state. A 300 mW 532 nm frequency-doubled Nd:YVO₄ pump laser beam and a 5 mW supercontinuum probe laser

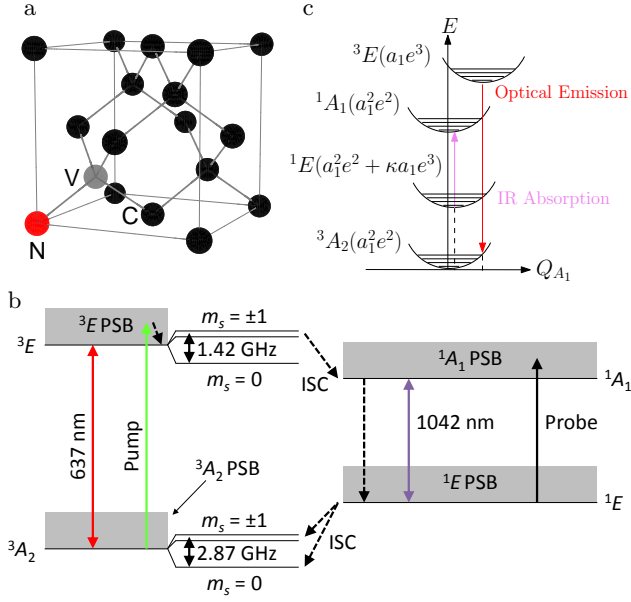


FIG. 1. (a) The diamond lattice structure, containing an NV center. (b) The NV⁻ energy-level diagram and our pump-probe spectroscopy scheme. The states are labeled by their C_{3v} representations and electron spin multiplicities. Solid arrows are optical and microwave transitions, and dashed arrows are non-radiative transitions. The label “ISC” indicates intersystem crossing, which occurs primarily for the 3E $m_s = \pm 1$ states and is responsible for optical pumping. (c) A configuration coordinate diagram for A_1 phonon modes showing the harmonic nuclear potential wells and phonon energy levels. The configuration for each electronic state is denoted in parentheses, and Q_{A_1} is the normalized nuclear coordinate. The 3A_2 and 1A_1 states should have $a_1^2e^2$ configuration, 3E should have a_1e^3 , and 1E should have a mixture of the two [25].

beam (wavelength range 450-1800 nm) were combined on a dichroic beamsplitter and focused with a $40\times$ microscope objective onto a cryogenically cooled diamond sample. The transmitted light was collimated and detected with a spectrometer with ~ 1 nm resolution. A chopper wheel modulated the pump light and a computer collected a transmission spectrum each time the pump light was blocked and unblocked. Absorption from 1E appeared as a difference between the “pump blocked” and “pump unblocked” supercontinuum transmitted intensities. In another experiment, we used 912 nm and 1042 nm continuous-wave (cw) lasers as probe sources and replaced the spectrometer with a photodiode [34].

Figure 3a shows the $^1E \rightarrow ^1A_1$ ZPL and PSB supercontinuum absorption spectrum taken at 10 K with the sample “B8”, a synthetic type Ib high-pressure, high-temperature (HPHT) diamond with ~ 10 ppm NV⁻ concentration. The PSB includes narrow absorption lines at 811 and 912 nm and broad absorption features at 872, 922, 931, and 983 nm. We believe the 811 and 912 nm lines are due to a 169.28(4) meV phonon mode and that

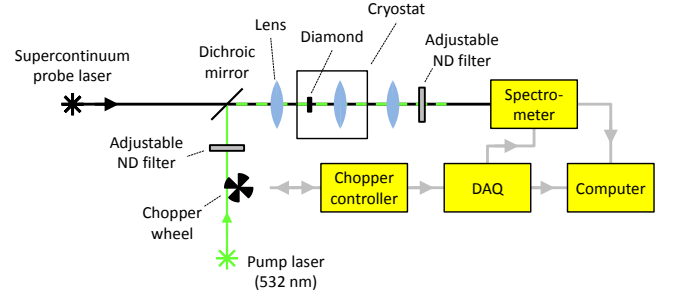


FIG. 2. The experimental apparatus. The data acquisition device (DAQ) monitors the chopper wheel state and triggers a spectrum acquisition when the pump is blocked or unblocked. The computer collects “pump blocked” and “pump unblocked” transmission spectra.

the other lines are due to a distribution of phonon modes. Figure 3b shows the $^3E \rightarrow ^3A_2$ fluorescence spectrum taken at 4 K with a similar diamond. This PSB has a broader energy range, and has features at 686, 692, and 696 nm. Using these measured spectra and the techniques outlined in Refs. [28, 34, 35], we calculated the $^1E \rightarrow ^1A_1$ and $^3E \rightarrow ^3A_2$ one-phonon spectra (Fig. 4), which are the rates at which these transitions create one phonon of a given energy. We expect these one-phonon spectra to be similar, since both come from $E \rightarrow A$ transitions with the same final-state electronic configuration (Fig. 1c). The one-phonon spectra show rough similarity, and the differences between them are because of higher-order corrections to the 1A_1 and 3A_2 electronic states.

We observed the above $^1E \rightarrow ^1A_1$ PSB features in several diamond samples, and the absorption was greater in samples with higher NV⁻ concentration. The $^1E \rightarrow ^1A_1$ absorption should increase with pump power and saturate when the pumping rate becomes comparable to the 1E decay rate. The absorption at room temperature increased linearly with pump power (up to 60 mW focused to a beam waist smaller than 5 μ m), indicating that the 1E population was not saturated. However, the absorption at 10 K saturated at ~ 15 mW. This saturation is likely due to the enhanced 1E lifetime at cold temperature [18]. Introducing a static transverse magnetic field to the samples improved the absorption contrast by a few percent. This is because the Zeeman interaction mixes the triplet spin sublevels, which spoils the optical pumping to $m_s = 0$ and increases the 1E population. We did not detect a $^1E \rightarrow ^1E'$ ZPL in the 480-1100 nm range of the supercontinuum transmission spectrum, which means this transition lies outside of this range or was too weak to detect. This wavelength span was limited by the spectrometer.

Using a rate equation calculation based on the NV⁻ excitation and decay rates at room temperature [33], we estimate the room temperature $^1E \rightarrow ^1A_1$ ZPL cross section to be roughly 4×10^{-22} m² [34], which is consis-

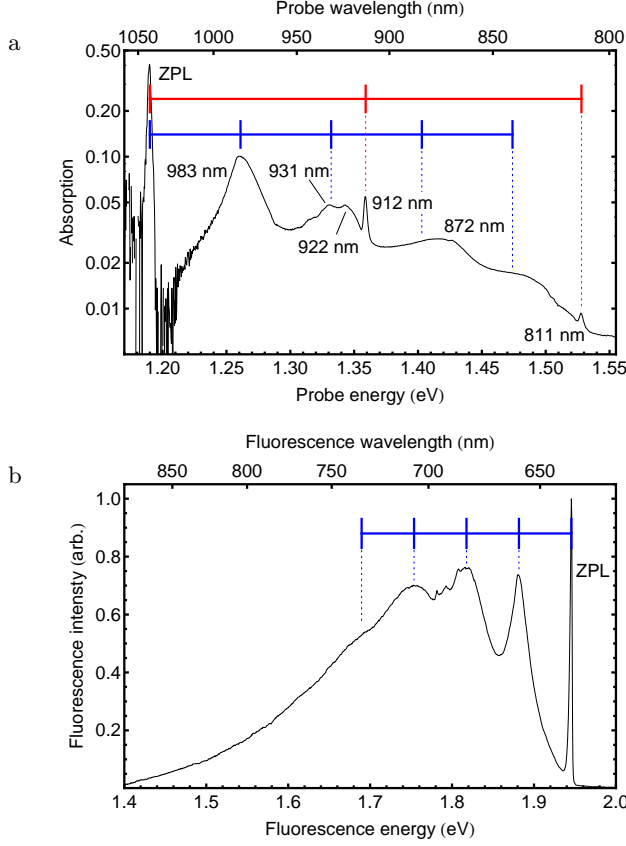


FIG. 3. (a) The supercontinuum absorption spectrum collected at 10 K for diamond sample B8 using 35 mW of pump-laser light. PSB fluorescence from ${}^3E \rightarrow {}^3A_2$ is present for wavelengths shorter than 840 nm and has been subtracted out. The horizontal lines indicate the expected PSB absorption energies for 71 and 169 meV phonons. (b) The fluorescence spectrum of a similar diamond collected at 4 K. The horizontal lines indicate the expected PSB absorption energies for 64 meV phonons. Although the 686, 692, and 696 nm features are often ignored, they are vital to our comparison of the ${}^1E \rightarrow {}^1A_1$ and ${}^3E \rightarrow {}^3A_2$ PSBs, as they give rise to peaks (3)-(5) in Fig. 4. From these plots, we calculated Huang-Rhys parameters of 0.9 (a) and 3.49 (b).

tent with previous work [36]. The accuracy of this cross section estimate is primarily limited by uncertainty in the NV^- concentration; varying the NV^- concentration from 5 to 20 ppm in our model yields estimated cross sections ranging from 3.4 to $5.4 \times 10^{-22} \text{ m}^2$ (compared to $4.0 \times 10^{-22} \text{ m}^2$ with 10 ppm NV^-).

We varied the temperature of sample B8 from 10 to 300 K and recorded the absorption-feature contrasts, linewidths, and integrated areas [34]. The features become weaker and broader with increasing temperature, and their integrated areas decrease. This decrease in area is consistent with the 1E lifetime decrease observed in Ref. [18].

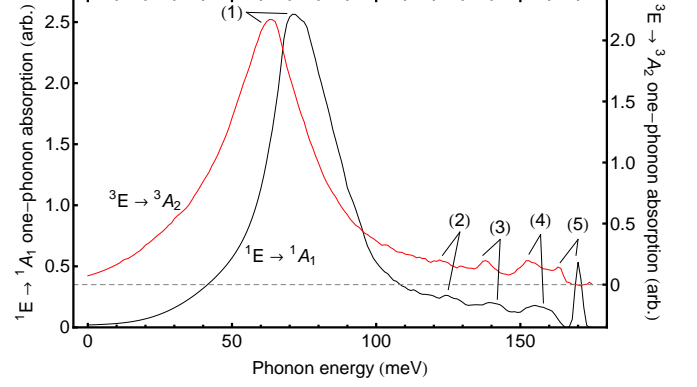


FIG. 4. The one-phonon spectra for the ${}^1E \rightarrow {}^1A_1$ and ${}^3E \rightarrow {}^3A_2$ transitions, extracted from Fig. 3. The above spectra are normalized to have equal areas, and the 3A_2 curve is vertically offset for clarity. In each spectrum we see five peaks, labeled (1)-(5), though the 1A_1 peaks are shifted to higher energies (see Tab. I).

Peak #	3A_2 state	1A_1 state
(1)	64 meV	71 meV
(2)	122 meV	125 meV
(3)	138 meV	141 meV
(4)	153 meV	156 meV
(5)	163 meV	169 meV

TABLE I. The energies of the one-phonon peaks shown in Fig. 4. When comparing the energies of the 3A_2 and 1A_1 phonon modes, we see a systematic shift to higher energy of a few meV.

Using cw probe lasers and a similar diamond sample “S2” (16 ppm NV^- concentration), we measured the center wavelengths of the 912 and 1042 nm absorption lines at 40 K to be 912.19(2) nm and 1041.96(2) nm. Our ZPL center wavelength is consistent with previous measurements [18, 19]. At low temperatures, the 1042 and 912 nm features have narrow widths (currently limited by the spectrometer resolution). These narrow widths imply that the vibrational mode associated with the 912 nm feature is sharp. By measuring 912 nm absorption as a function of light polarization angle, we found that the 912 nm absorption has the same polarization selection rules as the ${}^1E \rightarrow {}^1A_1$ ZPL [18, 34].

Comparing the ${}^1E \rightarrow {}^1A_1$ absorption PSB depicted in Fig. 3a with previous observations of the ${}^1A_1 \rightarrow {}^1E$ fluorescence PSB [19, 20], it is evident that these PSBs differ significantly. This difference is due to the anharmonicity of the 1E vibronic levels induced by the dynamic Jahn-Teller effect, which is not present in 1A_1 [20]. In the low-temperature limit, the PSB features of $A \rightarrow E$ electronic transitions will exhibit anharmonicity, while the PSB features of $E \rightarrow A$ transitions will be harmonic [37]. Consequently, it is appropriate to compare the ${}^1E \rightarrow {}^1A_1$

absorption PSB with the ${}^3E \rightarrow {}^3A_2$ fluorescence PSB. Furthermore, 1A_1 and 3A_2 have the same electronic configuration ($a_1^2e^2$), and hence should have the same nuclear equilibrium positions and phonon modes. Since their initial states are different, the ${}^1E \rightarrow {}^1A_1$ and ${}^3E \rightarrow {}^3A_2$ transitions may couple to a different number of phonon modes and have different Huang-Rhys parameters, but the 1A_1 and 3A_2 one-phonon spectra should be the same.

As mentioned above, we calculated the one-phonon spectra from the PSBs shown in Fig. 3. The n -phonon spectrum is the convolution of the $(n-1)$ -phonon and one-phonon spectra, and the sum of all n -phonon spectra generates the transition PSB. The one-phonon spectra are also related to the 1A_1 and 3A_2 phonon density of states (DOS). As seen in Fig. 4, we found similarities between the one-phonon spectra; both spectra have one large feature and four small features. However, all of the ${}^1E \rightarrow {}^1A_1$ features are displaced to higher energies (Tab. I).

Introducing a point defect into a lattice alters the vibrational motion of the defect and its neighbors from what it would have been with ordinary atoms in the lattice. This is because the parameters that determine the frequencies of the vibrational motion for these atoms (the masses and effective spring constants) are modified. When the frequencies of the local oscillations of the defect lie within the spectrum of allowed vibrational modes of the remaining crystal, the local modes hybridize with the lattice modes and are called “quasiloca” (quasiloca because the nuclear oscillation amplitudes fall off slowly with increasing distance from the defect) [30, 35]. The ~ 71 meV phonon modes we observed appear to be from a quasilocal mode of NV^- in the 1A_1 state. The diamond lattice phonon DOS is appreciable at 71 meV [38, 39], and since the NV^- 71 meV mode couples strongly to the diamond lattice modes, the peaks of the 71 meV mode are consequently broadened.

In contrast to the quasilocal mode case, when the frequency of the local oscillations of a defect lies outside the lattice phonon DOS, this yields a “localized” mode. In this instance, the oscillations of the defect couple poorly to the oscillations of the rest of the crystal, the vibrational motion is confined to the region of the defect, and the local phonon mode energy is unbroadened. This is the case for the 169 meV mode. The diamond lattice phonon DOS has an upper limit of 168 meV [38–40]. The NV^- 169 meV mode falls outside the diamond lattice phonon spectrum and couples poorly to the lattice modes, consequently making the peaks of the 169 meV mode in Fig. 3a sharp.

The existence of a 169 meV local phonon mode and the differences between the ${}^1E \rightarrow {}^1A_1$ and ${}^3E \rightarrow {}^3A_2$ one-phonon spectra are surprising for several reasons. *Ab initio* calculations for the NV^- triplet-state vibrations do not predict the existence of high-energy local phonon modes [29, 30], and the ${}^1E \rightarrow {}^1A_1$ PSB is the

only NV^- PSB to contain such a feature. Due to the discrepancy in one-phonon spectra, we conclude that the 1A_1 and 3A_2 levels have corrections to their lowest-order electronic states that affect the phonon modes of these states differently. Since the features in the one-phonon spectrum are shifted to higher energies, we can conclude that the nearby atoms are more tightly bonded in the 1A_1 state than in the 3A_2 state.

In summary, we measured the ${}^1E \rightarrow {}^1A_1$ absorption spectrum of the NV^- center using pump-probe spectroscopy. In the ${}^1E \rightarrow {}^1A_1$ PSB and one-phonon absorption spectrum we found several phonon modes, one of which lies outside the diamond lattice phonon DOS. The ${}^1E \rightarrow {}^1A_1$ and ${}^3E \rightarrow {}^3A_2$ one-phonon spectra show general similarities, but the 1A_1 phonon modes are shifted to higher energies, which is due to corrections to the 1A_1 and 3A_2 orbital configurations. We also searched for the ${}^1E \rightarrow {}^1E'$ ZPL for energies up to 2.0 eV, but we did not detect it. Since the ${}^1E \rightarrow {}^1A_1$ and ${}^1E \rightarrow {}^1E'$ transitions should have similar oscillator strengths, this suggests that the ${}^1E \rightarrow {}^1E'$ ZPL energy is greater than 2.0 eV. Follow-up experiments will extend the search for the ${}^1E \rightarrow {}^1E'$ ZPL to higher energies with improved sensitivity.

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Supplementary material to “The Infrared Absorption Band and Vibronic Structure of the Nitrogen-Vacancy Center in Diamond”

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INTRODUCTION

In this supplement we present additional content to the results described in the main article. We include additional experimental technical details and findings, a description of how we calculated the one-phonon spectra from the ${}^1E \rightarrow {}^1A_1$ and ${}^3E \rightarrow {}^3A_2$ absorption and emission PSBs, and an analysis of the resulting 3A_2 and 1A_1 vibronic bands.

EXPERIMENTAL DETAILS

We used an Olympus LUCPlanFL N 40x PH2 microscope objective to focus the pump and probe beams onto the diamond samples (to a beam waist smaller than 5 μm). This objective lens is achromatic, which ensures that the pumped NV^- and probe spatial regions overlap. We used a Janis ST-500 liquid-helium flow cryostat for cooling the diamond sample. Our pump-laser source was a Coherent Verdi-V6, and our cw probe-laser sources included 2 mW of 912 nm light from a Coherent CR 899 Ti:Sapphire laser, 30 mW of 912 nm light from a diode laser (1 nm linewidth), and 1.5 mW of 1042 nm light from an external-cavity diode laser (ECDL). We used a Fianium SC450-2 supercontinuum laser as our broadband probe and a Ocean Optics USB2000+VIS-NIR (~ 1 nm resolution, optimized for infrared sensing) for detecting transmitted supercontinuum light.

We used the ${}^3E \rightarrow {}^3A_2$ fluorescence spectrum of a similar diamond sample at 4 K for comparison with our ${}^1E \rightarrow {}^1A_1$ spectrum. This sample was also illuminated with 532 nm pump light, and the emitted fluorescence was dispersed with a monochromator (0.1 nm resolution) and detected with a cooled-Ge detector (calibrated with the blackbody spectrum from a 3100 K tungsten bulb). Although we compared spectra from different diamond samples, the spectra from different high-concentration samples are in general consistent.

$^1E \rightarrow ^1A_1$ ZPL CROSS SECTION ESTIMATE

Using decay-rate and pump-laser absorption cross section parameters determined in [1, 2], we constructed a rate equation model to estimate the fraction of NV^- centers in the metastable state throughout the diamond sample, from which we estimated the $^1E \rightarrow ^1A_1$ ZPL cross section at room temperature. This model takes into account the pump beam divergence and absorption in the diamond. Using this calculation of the metastable NV^- center density and the experimentally determined 1042 nm transmission in sample B8 at various pump powers, we determined the $^1E \rightarrow ^1A_1$ ZPL cross section. For simplicity, we approximated the probe beam to be a straight line through the pump beam axis. We estimated a $^1E \rightarrow ^1A_1$ ZPL cross section of $4 \times 10^{-22} \text{ m}^2$. This estimate is consistent with that of Ref. [3]. As mentioned in the main text, the uncertainty in NV^- center concentration dominates the error on this cross section estimate. Uncertainty in the NV^- center excited-state decay rates [1], the pump-laser absorption cross section [2], the pump beam waist, and the distance between the pump beam focus and the diamond surface contribute an additional uncertainty of about $0.9 \times 10^{-22} \text{ m}^2$.

TEMPERATURE DEPENDENCE OF THE $^1E \rightarrow ^1A_1$ ZPL AND PSB

We measured $^1E \rightarrow ^1A_1$ supercontinuum absorption spectra while varying the temperature of sample B8 from 10 to 300 K. Figure S1 shows the absorption, linewidths, and integrated areas for the 1042 nm ZPL and the 811, 912, and 983 nm PSB features. These features became weaker and broader with increasing temperature, and the integrated areas decreased. The integrated areas should be independent of temperature [4]. However, the 1E state has shorter lifetime at higher temperature due to the enhanced electron-phonon decay rate to 3A_2 [5]. We believe the decrease in integrated area is because of the consequent reduction in 1E population at higher temperature.

912 NM POLARIZATION SELECTION RULES

We investigated the light-polarization selection rules for 912 nm absorption and compared them to those listed in Table S1. An $E \rightarrow A_1$ transition is dipole-allowed for (x, y) -polarized light, while an $E \rightarrow E$ transition is also dipole-allowed for z -polarized light. A difference

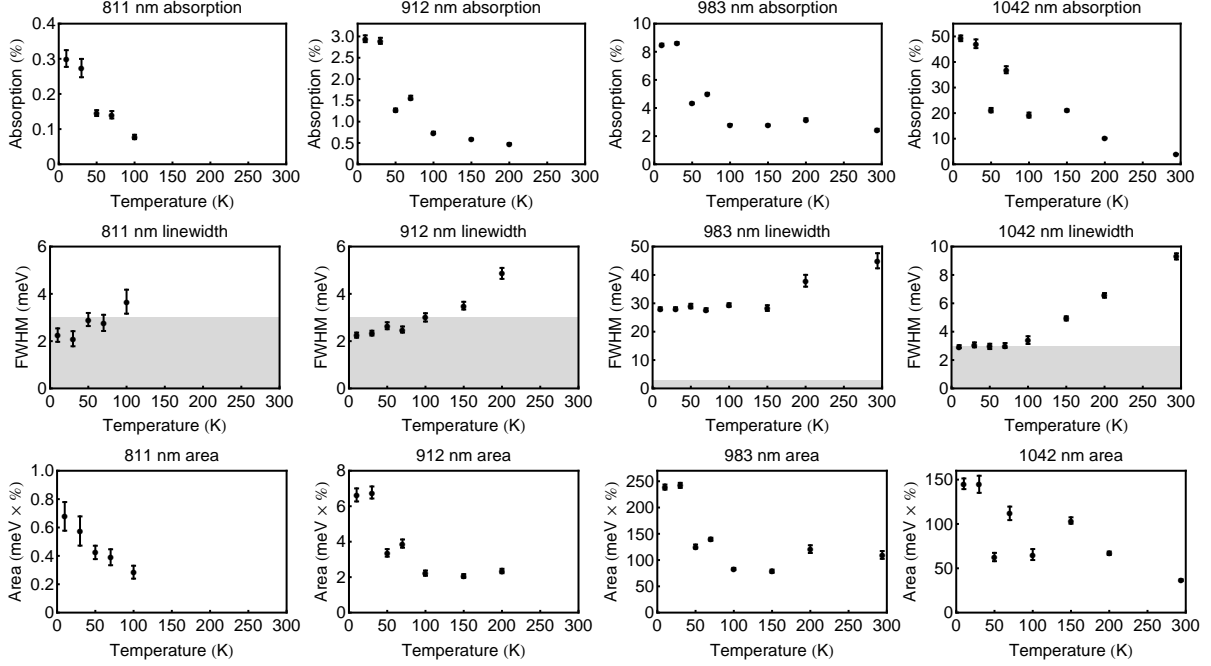


FIG. S1. The percent absorption, linewidth, and integrated area of ${}^1E \rightarrow {}^1A_1$ absorption features in sample B8 as a function of temperature. The 811 and 912 nm lines vanished in the supercontinuum absorption spectra above 100 and 200 K, respectively. The spectrometer resolution contributes to the apparent linewidths plotted above; the gray region (3 meV) indicates where the spectrometer instrument broadening significantly contributes to the measured linewidths. We believe the 50 K and 90 K measurements to be outliers due to thermal expansion in the cryostat during the measurement. The above error bars are one-sigma statistical errors extracted from the parameter fits of the absorption spectra. We estimate a 1 meV systematic uncertainty on the above linewidths.

between the 912 nm selection rules and the expected $E \rightarrow A_1$ ZPL selection rules could indicate that the 912 nm line is an $E \rightarrow E$ transition or that the ${}^1E \rightarrow {}^1A_1$ selection rules are not strictly obeyed in PSB transitions [5]. We determined the polarization dependence of 912 nm absorption in a room-temperature optically-detected magnetic resonance (ODMR) experiment with diamond sample S2. We singled out the [111]-oriented NV^- centers with an axial 15 G static magnetic field, exposed the sample to microwaves from a nearby wire, and measured the diode-laser absorption as a function of microwave frequency. Microwaves resonant with ${}^3A_2 m_s = 0 \rightarrow m_s = \pm 1$ transitions spoil the optical spin polarization, increase 1E population, and enhance probe absorption. By measuring the $m_s = 0 \rightarrow m_s = \pm 1$ absorption in [111]-oriented centers as a function of polarization angle for probe-light wavevector \hat{k} parallel and perpendicular to the [111] z -axis, we found that the 912

nm transition is (x, y) -allowed and z -forbidden (Fig. S2). These selection rules indicate an $E \rightarrow A_1$ transition and are consistent with the ${}^1E \rightarrow {}^1A_1$ ZPL selection rules [5]. We performed this experiment at 40 K with the 912 nm Ti:Sapphire laser and obtained consistent results for $\hat{k} \parallel z$, but we were unable to test $\hat{k} \perp z$ because of mechanical constraints.

Transition	Dipole-allowed
$A_1 \leftrightarrow A_1$	z
$A_1 \leftrightarrow A_2$	—
$A_1 \leftrightarrow E$	x, y
$A_2 \leftrightarrow A_2$	z
$A_2 \leftrightarrow E$	x, y
$E \leftrightarrow E$	x, y, z

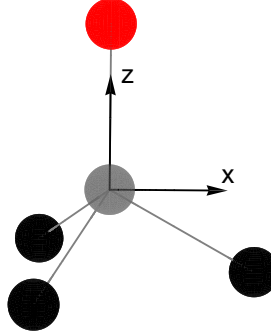


TABLE S1. Photon polarizations for dipole-allowed transitions between C_{3v} electronic states [4]. The notation “ x, y ” implies that any polarization in the x - y plane has the same transition amplitude. The drawing on the right indicates the choice of axes.

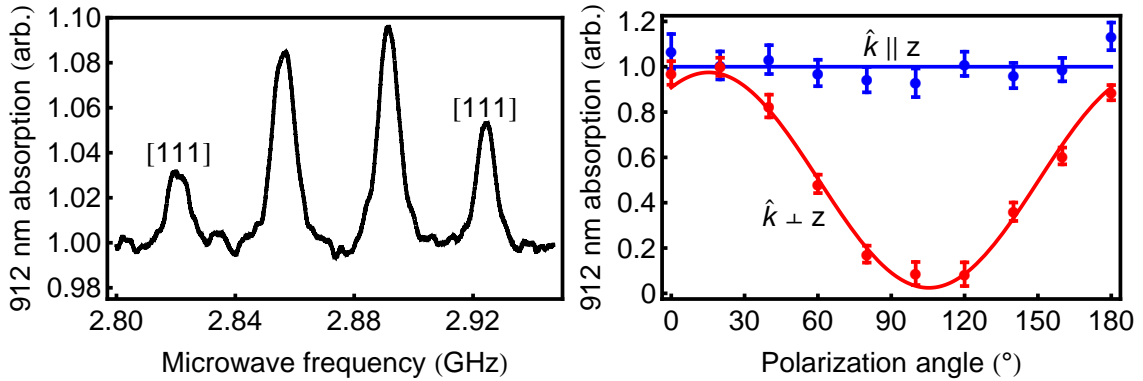


FIG. S2. (Left) A sample ODMR spectrum ($\hat{k} \perp z$) taken at room temperature, with absorption peaks for [111]-oriented centers labeled. The middle two peaks are due to the other three orientations. (Right) 912 nm absorption by [111]-oriented centers at different light polarization angles. The $\hat{k} \parallel z$ case is only sensitive to x, y polarization while the $\hat{k} \perp z$ case is also sensitive to z polarization. The constant nonzero $\hat{k} \parallel z$ ODMR peak height and sinusoidal variation to 0 in the $\hat{k} \perp z$ data indicate the transition is (x, y) -allowed and z -forbidden.

VIBRONIC ANALYSIS

The vibronic structure predicted by the current NV^- model

By adopting the adiabatic and harmonic approximations, the nuclear vibrational motion associated with a given electronic state is approximately governed by the harmonic potential formed by the dependence of the state's electronic energy on the nuclear coordinates. The nuclear vibrational potential associated with the n^{th} electronic state $|\Phi_n\rangle$ is [6]

$$E_n(\vec{Q}) = E_n(0) + \sum_{\alpha,j,k} a_{n,\alpha,j,k} Q_{\alpha,j,k} + \frac{1}{2}(\omega_{\alpha,j,k}^2 + b_{n,\alpha,j,k}) Q_{\alpha,j,k}^2 \quad (1)$$

$$= E_n(0) - \delta E_n(0) + \frac{1}{2} \sum_{\alpha,j,k} (\omega_{\alpha,j,k}^2 + b_{n,\alpha,j,k}) (Q_{\alpha,j,k} - \delta Q_{n,\alpha,j,k})^2, \quad (2)$$

where

$$\begin{aligned} E_n(0) &= \langle \Phi_n | \hat{H}_e | \Phi_n \rangle \\ a_{n,\alpha,j,k} &= \langle \Phi_n | \left. \frac{\partial \hat{H}_e}{\partial Q_{\alpha,j,k}} \right|_0 | \Phi_n \rangle \\ \omega_{\alpha,j,k}^2 &= \langle \Phi_0 | \left. \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,j,k}^2} \right|_0 | \Phi_0 \rangle \\ b_{n,\alpha,j,k} &= \langle \Phi_n | \left. \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,j,k}^2} \right|_0 | \Phi_n \rangle - \omega_{\alpha,j,k}^2 \\ \delta E_n(0) &= \sum_{\alpha,j,k} \frac{a_{n,\alpha,j,k}^2}{2(\omega_{\alpha,j,k}^2 + b_{n,\alpha,j,k})} \\ \delta Q_{n,\alpha,j,k} &= -\frac{a_{n,\alpha,j,k}}{2(\omega_{\alpha,j,k}^2 + b_{n,\alpha,j,k})}. \end{aligned} \quad (3)$$

In the above expressions, \hat{H}_e is the electronic Hamiltonian, $Q_{\alpha,j,k}$ is the normal nuclear displacement coordinate (with respect to the nuclear equilibrium coordinates of the ground $n = 0$ electronic state) of the α^{th} ground electronic state eigenmode with symmetry $(j, k) = \{A_1, A_2, (E, x), (E, y)\}$ and vibrational energy $\hbar\omega_{\alpha,j,k}$. Note that quadratic terms that couple the eigenmodes in excited electronic states have been ignored and that for the ground electronic state $a_{0,\alpha,j,k} = 0$ is a condition of nuclear equilibrium. It is clear that linear interactions displace the nuclear equilibrium coordinates by $\delta Q_{n,\alpha,j,k}$ and that the quadratic interactions shift the vibrational energies by $\delta\omega_{n,\alpha,j,k} \approx b_{n,\alpha,j,k}/2$.

The vibrational state $|\chi_{n,\nu}\rangle$ associated with the n^{th} electronic state with vibronic energy

$E_{n,\nu}$ follows trivially from the vibrational equation $[\hat{T}(\vec{Q}) + E_n(\vec{Q})] |\chi_{n,\nu}\rangle = E_{n,\nu} |\chi_{n,\nu}\rangle$, where $\hat{T}(\vec{Q})$ is the nuclear kinetic energy. Importantly, the vibronic coupling of the adiabatic vibronic states $|\Phi_n, \chi_{n,\nu}\rangle$ by Jahn-Teller interactions between degenerate electronic states has not been considered thus far. The Jahn-Teller interactions occur between degenerate electronic states and degenerate phonon modes and result in anharmonicities in the vibronic structures of the degenerate electronic states. For the case of the NV^- center, only E -symmetric electronic states and phonon modes exhibit degeneracy. As discussed in the article, the vibronic couplings and anharmonicities induced by the Jahn-Teller effect are not relevant to the PSBs analyzed in this work.

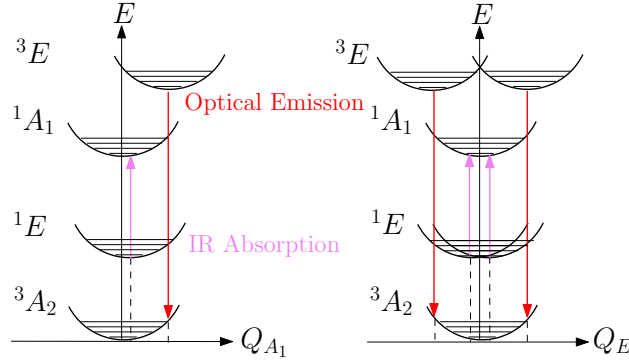


FIG. S3. (color online) Configuration coordinate diagrams for A_1 (Q_{A_1}) and E (Q_E) phonon modes depicting the harmonic nuclear potential wells and phonon energy levels. The optical emission and IR absorption transitions (solid arrows) are depicted according to the Franck-Condon principle. The current model predicts that the wells of the 3E and 1E are displaced from the 3A_2 equilibrium coordinates (as indicated by dashed lines) differently, but the well of 1A_1 is not displaced. The displacements of the degenerate electronic levels of 3E and 1E are equal and opposite (displacements do not imply static Jahn-Teller effects). The current model also predicts that the phonon energies of 3E and 1E , but not 1A_1 , may differ from 3A_2 .

To elaborate on this discussion, the IR absorption and optical emission PSBs are both $E \rightarrow A$ electronic transitions and thus have analogous configuration coordinate diagrams (refer to Fig. S3). At low temperatures where only the ground vibronic levels of 3E and 1E are populated, the features of the PSBs occur at the harmonic vibronic energies of 3A_2 and 1A_1 and are unaffected by the Jahn-Teller anharmonicities of 3E and 1E . Furthermore, for typical Jahn-Teller interactions, the contributions of E modes to PSBs of $E \rightarrow A$ electronic transitions are well described by the techniques applied to model A_1 mode contributions [7]. It follows that a comparison of the PSBs can relate the vibronic structures of 3A_2 and 1A_1 and also the electron-phonon interactions that give rise to the PSBs.

In the low-temperature limit, the Huang-Rhys parameter of a transition between the ground and n^{th} excited electronic states is given by [6, 8]

$$S_n = \sum_{\alpha,j,k} \frac{\delta E_{n,\alpha,j,k}}{\hbar\omega_{n,\alpha,j,k}} \approx \int_0^\Omega S_n(\omega)\rho(\omega) d\omega, \quad (4)$$

where $\rho(\omega)$ is the density of modes of the ground electronic state, Ω is the highest mode frequency, and (ignoring mode energy shifts) $S_n(\omega) = \overline{a_n^2}(\omega)/2\hbar\omega^3$, such that $\overline{a_n^2}(\omega)$ is the average squared linear interaction parameter of all modes with frequency ω . Likewise, the bandshape function due to linear interactions only is [6, 8]

$$g_n(\omega) = N_n S(\omega)\rho(\omega), \quad (5)$$

where N_n is a normalization constant satisfying $N_n \int_0^\Omega g(\omega) d\omega = 1$. Note the minor differences in the above expressions to those that appear in Refs. [6] and [8].

Using the well-established expressions of the NV^- electronic states in terms of molecular orbitals (MOs) (a_1 , e_x and e_y) [9], the linear and quadratic interaction parameters may be derived for each of the NV^- center's electronic levels correct to second-order in electron-electron electrostatic interaction (refer to Table S2). Note that only the 1E and $^1E'$ levels couple due to the electrostatic interactions and this coupling can be described by the parameter κ [9]. Table S2 clearly demonstrates that the current theoretical model predicts that the vibrational parameters of 1A_1 do not differ from those of 3A_2 , whereas the parameters do differ at zero-order for 3E and at first- (linear interactions with E modes) and second-order (linear interactions with A_1 modes and all quadratic interactions) in κ for 1E . These results are depicted in Fig. S3. As the parameters of 1A_1 do not differ from the ground electronic level, the above expressions for S_n and $g_n(\omega)$ corresponding to a transition involving the ground electronic level may also apply to a transition involving 1A_1 . Thus, the current model predicts that A_1 and E modes contribute linearly at zero-order to the S and $g(\omega)$ of the NV^- optical emission PSB, but that A_1 and E modes contribute linearly at different orders in κ (second- and first-orders, respectively) to the IR absorption PSB.

In summary, the current theoretical model predicts that the mode energies of 1A_1 and 3A_2 are the same (i.e. no mode energy shift) and that the contributions of A_1 and E modes to the optical emission and IR absorption bandshape functions should differ and result in

different PSB features. Both of these predictions disagree with the observations made in this work. Resolution of this disagreement requires further development of the current molecular model of the NV^- center.

Decomposition and analysis of the vibronic bands

Adopting the well-established techniques that were introduced by Maradudin [10] and applied extensively by Davies [8] to color centers in diamond, the normalized PSB $I(\omega)$ of an electronic transition can be described by

$$\begin{aligned} I(\omega) &= e^{-S} \int_{-\infty}^{\infty} e^{-\gamma|t|} e^{Sg(t)} e^{i\omega t} dt \\ &= e^{-S} I_0(\omega) + e^{-S} \sum_{n=1}^{\infty} \frac{S^n}{n!} I_0 \otimes I_n(\omega), \end{aligned} \quad (6)$$

where S is the Huang-Rhys parameter, γ is the homogeneous ZPL width, I_0 is the homogeneous ZPL shape (as parameterized by γ), $g(t) = (1/2\pi) \int_{-\Omega}^{\Omega} g(\omega) e^{-i\omega t} d\omega$ is the bandshape function, $I_1(\omega) = g(\omega)$ if $-\Omega \leq \omega \leq \Omega$ and $= 0$ otherwise, $I_n = I_1 \otimes I_{n-1}(\omega)$ for $n > 1$, Ω is the highest phonon frequency of diamond, and \otimes denotes the operation of convolution. Note that the individual band components $I_n(\omega)$ offer the insightful interpretation of being representative of all processes of net energy $\hbar\omega$ involving the creation and/or annihilation of n phonons. The total PSB is thus the summation over all n -phonon processes.

Absorption $I_{\text{abs.}}(\omega)$ and emission $I_{\text{em.}}(\omega)$ spectra are related to the normalized PSB via

$$\frac{I_{\text{abs.}}(\omega_0 + \omega)}{\omega_0 + \omega} \propto \frac{I_{\text{em.}}(\omega_0 - \omega)}{(\omega_0 - \omega)^3} \propto I(\omega), \quad (7)$$

where $\hbar\omega_0$ is the ZPL energy. The normalization condition $\int_{-\infty}^{\infty} I(\omega) d\omega = 1$ ensures that knowledge of the proportionality factors is not required to obtain the normalized PSB from absorption/emission spectra. Once normalized, the Huang-Rhys parameter can be simply evaluated using $S = -\log \langle I_0 \rangle$, where $\langle I_0 \rangle$ is the integrated area of the ZPL. By applying Fourier techniques, the following expression for the bandshape function can be derived

$$g(\omega) = \frac{1}{S} \int_{-\infty}^{\infty} \log\{e^S e^{\gamma|t|} \int_{-\infty}^{\infty} [I(\omega) - e^{-S} I_0(\omega)] e^{-i\omega t} d\omega + 1\} e^{i\omega t} dt. \quad (8)$$

The above expression was found to be non-trivial to evaluate numerically and particularly

sensitive to spectral noise. Consequently, it could not be employed to directly obtain the optical emission and IR absorption bandshapes. After smoothing the spectra and evaluating approximate bandshape functions using the above expression, the evaluated bandshape functions were then used as seed functions to the iterative process first described by Mostoller *et al.* [11]. The process involves the calculation of each of the normalized PSB components $I_n(\omega)$ via convolutions of a seed $I_1(\omega)$ and then using

$$I_1(\omega) = e^S I(\omega) - I_0(\omega) - \sum_{n=2}^{\infty} \frac{S^n}{n!} I_0 \otimes I_n(\omega) \quad (9)$$

to obtain an improved estimate of $I_1(\omega)$. If a reasonable seed bandshape function was obtained directly from (8), we found that the iterative process would converge within only a few iterations.

The fitted IR absorption and optical emission PSBs, together with their individual band components $I_n(\omega)$, are depicted in Fig. S4 and Fig. S5, respectively. The plots demonstrate that the calculated PSBs reproduce all of the key features of the observed PSBs, but minor differences appear towards higher energy. These differences are more pronounced for the IR absorption PSB and are likely to be related to the origins of the unexpected phonon energy shifts of 1A_1 and/or the Jahn-Teller effect in 1E . Further investigation is required. As concluded in the article, the features of the optical emission and IR absorption PSBs result from electron-phonon interactions with similar phonon modes and that the mode energies are greater in 1A_1 than in 3A_2 . It was further concluded that the upward energy shift of the phonon modes in the 1A_1 level has resulted in a local mode appearing with an energy greater than those of the diamond lattice.

Analysis of the PSBs via a comparison with the phonons of diamond

Having established the relationships between the PSBs, it is left to explain the origins of the PSB features. If one assumes that in 3A_2 , the NV^- center only slightly perturbs the phonon modes of perfect diamond, one can explain the features of the optical $g(\omega)$ via a comparison with the diamond phonon dispersion curves along high symmetry directions ([111], [100] and [110]) and the phonon density of states (DOS). As the NV^- electronic charge is centered on the nearest-neighbor nuclei of the vacancy (NNV), it is expected that

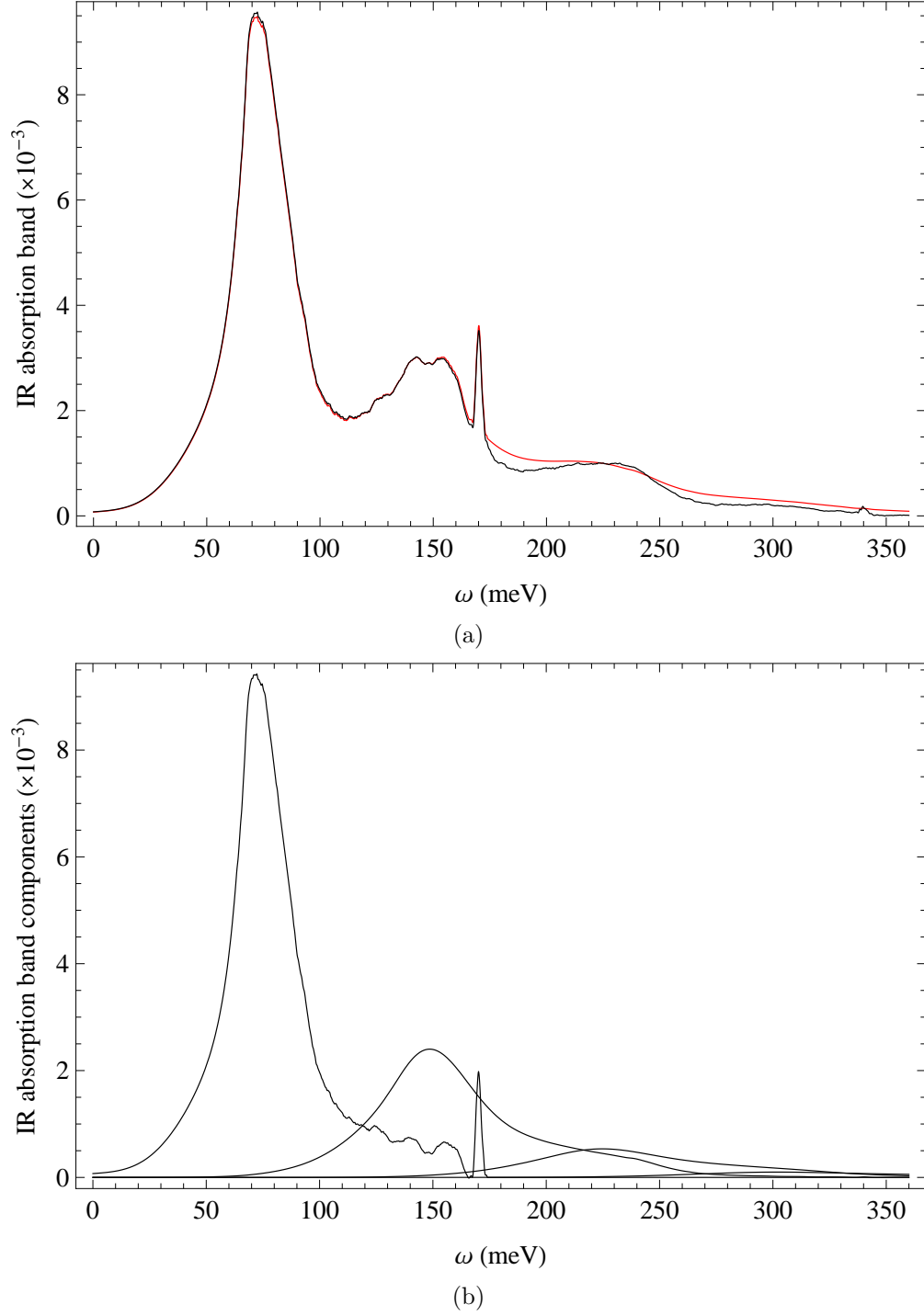


FIG. S4. (color online) (a) The normalized observed IR absorption PSB (black) and the calculated PSB (red) obtained using the IR absorption $g(\omega)$ and (6). (b) The calculated n -phonon components (increasing from $n=1$ from left to right) of the IR absorption PSB. The sum of the components equals the calculated PSB depicted in (a).

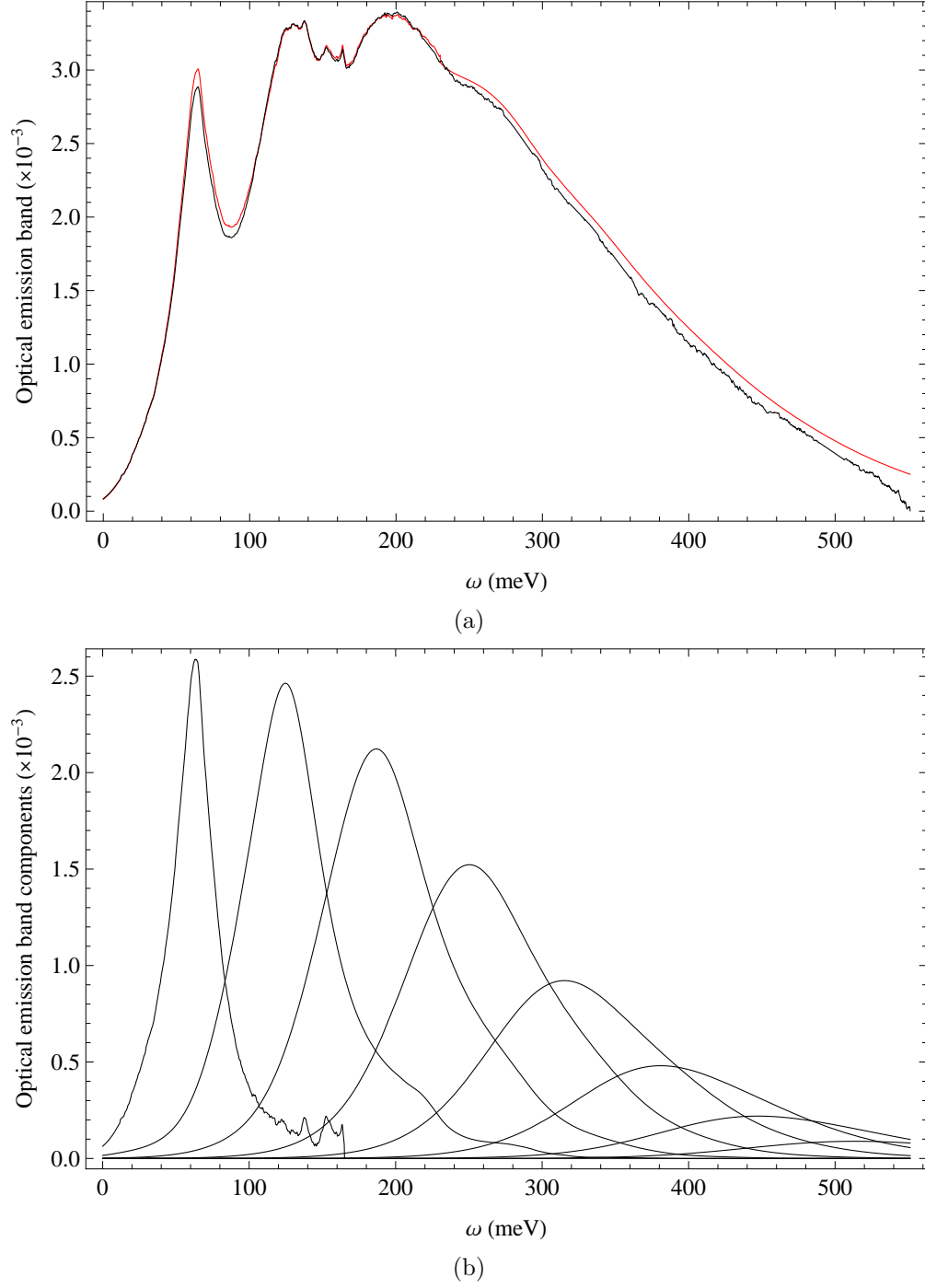


FIG. S5. (color online) (a) The normalized observed optical emission PSB (black) and the calculated PSB (red) obtained using the optical emission $g(\omega)$ and (6). (b) The calculated n -phonon components (increasing from $n=1$ from left to right) of the optical emission PSB. The sum of the components equals the calculated PSB depicted in (a).

the NV^- center will interact strongly with modes where the NNV undergo the largest relative displacement, which occurs when the NNV vibrate directly out of phase. As the NNV occupy equivalent Bravais lattice sites, this phase condition can be expressed as $\vec{k} \cdot \vec{R} = \pi$, where \vec{k} is the phonon wavevector and \vec{R} is the lattice vector connecting two NNV. For a given phonon wavevector direction, the phase condition is satisfied by a single wavevector magnitude. The magnitudes corresponding to the [111], [100] and [110] directions are $k = \frac{a}{R}$, $\frac{a}{R}$ and $\frac{2a}{3R}$, respectively, where a is the distance between equivalent Bravais lattice sites in the perfect diamond lattice and R is the distance between two NNV.

As expected, Fig. S6a shows that features of the optical $g(\omega)$ approximately correspond to features in the DOS and to points along the phonon dispersion curves at which the wavevector in the [111] direction has a particular magnitude. Fig. S6 also depicts similar comparisons with the [100] and [110] dispersion curves. By considering all of the comparisons together, it is clear that one can attribute all of the optical $g(\omega)$ features to points along the phonon dispersion curves whose wavevector magnitudes are related by the parameter $R/a \sim 1.2$. This semi-empirical result is in reasonable agreement with the ratios $R/a \sim 1.1 - 1.3$ obtained in previous *ab initio* calculations [12, 13]. Hence, the elements of the 1A_1 and 3A_2 vibronic structures observed in the IR absorption and optical emission PSBs can be directly related to specific phonon subgroups of diamond.

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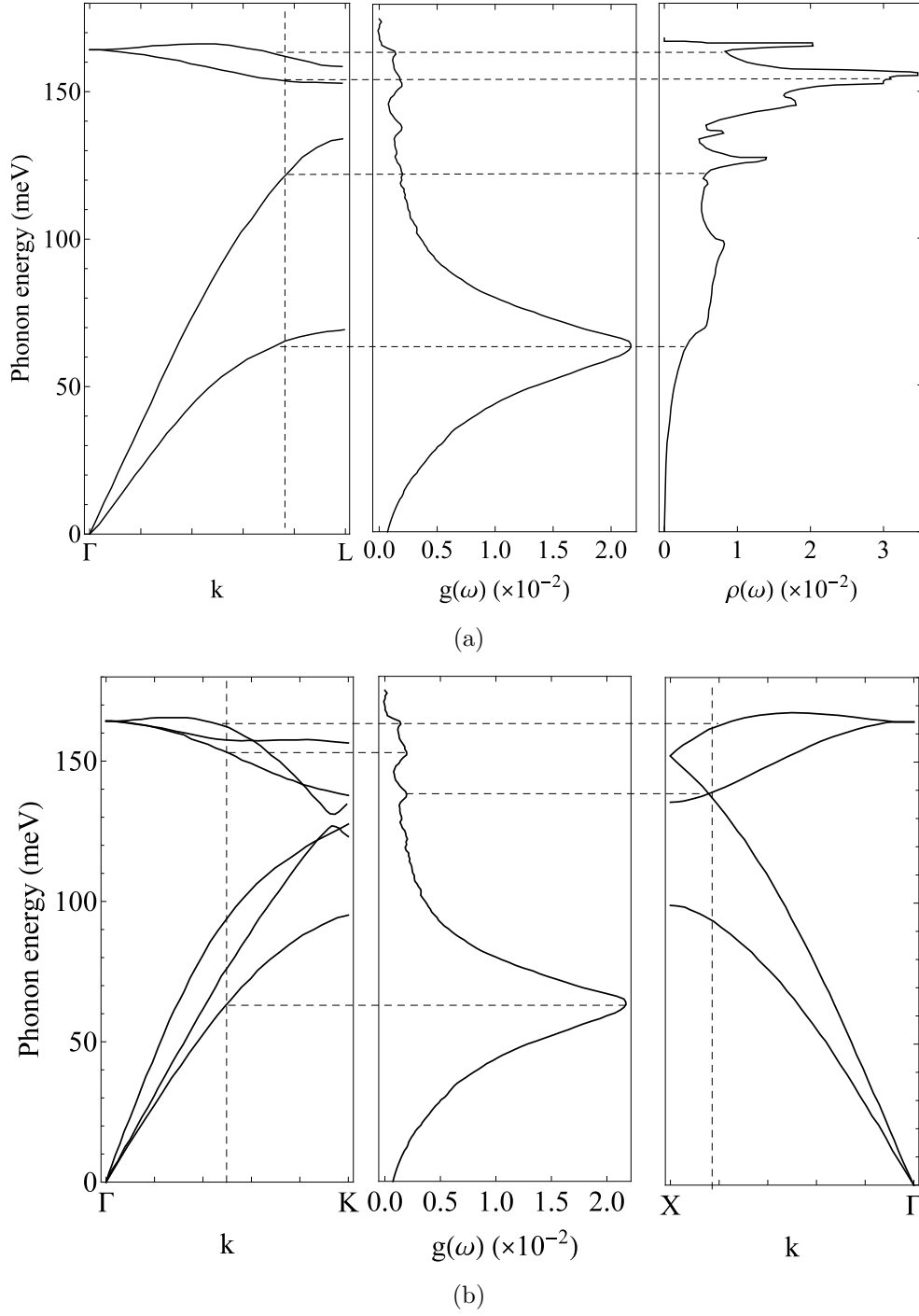


FIG. S6. (a) The comparison of the optical emission $g(\omega)$ with the perfect diamond phonon DOS $\rho(\omega)$ [14] and dispersion curves of phonons with wavevectors in the [111] direction [14]. (b) comparison with the dispersion curves of phonons with wavevectors in the [110] direction (left) and [100] direction (right) [14]. Horizontal dashed lines connect related features in adjacent plots and the vertical dashed line connects points with the same wavevector magnitude.

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TABLE S2. The vibrational parameters of the NV^- center's electronic levels as derived using the current model of the center. The parameters are expressed in terms of the Coulomb coupling parameter κ (refer to [9] for further details) and molecular orbital reduced matrix elements of the linear and quadratic electron-phonon interactions. The explicit expressions for the reduced matrix elements are contained in Table S3.

	3A_2	1E_x	1E_y	1A_1	3E_x	3E_y
a_{n,α,A_1}	0	$\kappa^2 a_{\alpha,A_1}$	$\kappa^2 a_{\alpha,A_1}$	0	a_{α,A_1}	a_{α,A_1}
a_{n,α,A_2}	0	0	0	0	0	0
$a_{n,\alpha,E,x}$	0	$2\kappa a_{\alpha,2,E}$	$-2\kappa a_{\alpha,2,E}$	0	$a_{\alpha,1,E}$	$-a_{\alpha,1,E}$
$a_{n,\alpha,E,y}$	0	0	0	0	0	0
b_{n,α,A_1}	0	$\kappa^2 b_{\alpha,A_1}$	$\kappa^2 b_{\alpha,A_1}$	0	b_{α,A_1}	b_{α,A_1}
b_{n,α,A_2}	0	$\kappa^2 b_{\alpha,A_2}$	$\kappa^2 b_{\alpha,A_2}$	0	b_{α,A_2}	b_{α,A_2}
$b_{n,\alpha,E,x}$	0	$\kappa^2 b_{\alpha,E}$	$\kappa^2 b_{\alpha,E}$	0	$b_{\alpha,E}$	$b_{\alpha,E}$
$b_{n,\alpha,E,y}$	0	$\kappa^2 b_{\alpha,E}$	$\kappa^2 b_{\alpha,E}$	0	$b_{\alpha,E}$	$b_{\alpha,E}$

TABLE S3. The reduced matrix elements of the linear and quadratic electron-phonon interactions expressed in terms of the NV^- center's molecular orbitals (a_1 , e_x and e_y). Refer to [9] for further details of the molecular orbitals and calculation of reduced matrix elements.

a_{α,A_1}	=	$\langle e \frac{\partial \hat{H}_e}{\partial Q_{\alpha,A_1}} \Big _0 e \rangle - \langle a_1 \frac{\partial \hat{H}_e}{\partial Q_{\alpha,A_1}} \Big _0 a_1 \rangle$
$a_{\alpha,1,E}$	=	$\langle e \frac{\partial \hat{H}_e}{\partial Q_{\alpha,E}} \Big _0 e \rangle$
$a_{\alpha,2,E}$	=	$\langle a_1 \frac{\partial \hat{H}_e}{\partial Q_{\alpha,E}} \Big _0 e \rangle$
b_{α,A_1}	=	$\langle e \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,A_1}^2} \Big _0 e \rangle - \langle a_1 \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,A_1}^2} \Big _0 a_1 \rangle$
b_{α,A_2}	=	$\langle e \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,A_2}^2} \Big _0 e \rangle - \langle a_1 \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,A_2}^2} \Big _0 a_1 \rangle$
$2b_{\alpha,E}$	=	$\langle e \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,E,x}^2} \Big _0 + \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,E,y}^2} \Big _0 e \rangle - \langle a_1 \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,E,x}^2} \Big _0 + \frac{\partial^2 \hat{H}_e}{\partial Q_{\alpha,E,y}^2} \Big _0 a_1 \rangle$